FINAL REPORT

Remediation of Explosives in Groundwater Using Zero-Valent Iron *In Situ* Treatment Wells

ESTCP Project ER-0223

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Rick Johnson
Paul Tratnyek
Oregon Health and Science University

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LIST OF ACRONYMS

ADNT	Aminodinitrotoluene
ASTM	American Standard for Testing and Materials
bgs	below ground surface
Br^-	Bromide
CAAP	Cornhusker Army Ammunition Plant
COC	chain of custody
Cl^-	Chloride
DQO	Data Quality Objectives
DQI	Data Quality Indicators
DoD	Department of Defense
DoE	Department of Energy
DO	dissolved oxygen
EHSC	Environmental Health and Safety Coordinator
ESTCP	Environmental Security Technology Certification Program
EPA	Environmental Protection Agency
EW	Extraction Well
Fe	Iron
Ft bgs	feet below ground surface
FID	Flame Ionization Detector
GC/MS	gas chromatograph/mass spectrometry
gpm	gallons per minute
HASP	Health and Safety Plan
HDPE	High Density Polyethylene
HMX	cyclotetramethylenetetranitramine
IC	Ion Chromatography
ID	Inside Diameter
ISTW	In situ treatment well
IW	Injection Well
kg	kilogram
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
mL	milliliters
MSDS	Material Safety Data Sheet
MS/MSD	matrix spike/matrix spike duplicate
MW	Monitoring Well
O&M	operations and maintenance
ORP	Oxidation Reduction Potential
OSHA	Occupational Safety and Health Administration
PARCC	precision, bias, accuracy, representativeness, completeness, and comparability
PID	Photoionization Detector
ppb	parts per billion
PPE	Personal Protective Equipment
PRB	permeable reactive barriers
PTA	Pilot Test Area
PVC	Polyvinyl Chloride
QAPP	Quality Assurance Project Plan

QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RDX	hexahydro-1, 3, 5-trinitro-1,3,5-triazine
RPD	Relative Percent Difference
RPM	Remedial Project Manager
SAP	Sampling and Analysis Plan
SERDP	Strategic Environmental Research and Development Program
SHSO	Site Health and Safety Officer
SO_4^-	Sulfate
TAT	triaminotoluene
TNT	2,4,6-trinitrotoluene
USEPA	United States Environmental Protection Agency
XPS	x-ray photoemission spectroscopy
ZVI	Zero-valent iron

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EXECUTIVE SUMMARY

The effectiveness of zero-valent iron (ZVI) permeable reactive barriers (PRB) for removal of explosives from groundwater has been recently demonstrated (ESTCP, 2007). However, cost-effective installation of ZVI PRB is typically limited to ~70 feet below ground surface. For sites where contamination is present at depths greater than is practical with conventional PRB, well-based technologies are appropriate. This can, for example, involve the injection of materials (e.g., nano iron, carbon substrates, etc.)

Demonstration Design

This report evaluates an approach in which granular iron was placed outside of the well screens in a pair of dual-screened wells. The wells were installed inside a large diameter temporary casing such that the iron adjacent to the upper and lower screens could be isolated from one another in a manner which would promote groundwater circulation between the pair of dual-screened wells.

Summary of Results

The groundwater hydrology of the well pair was evaluated, and met design expectations. A primary concern in the methodology was that water entering the treatment zone would contain materials (e.g., sulfate) that would plug the treatment zone over time. Based on our calculations for the site, this was not expected to be a problem, which turned out to be the case. Unfortunately, an unanticipated problem arose in which water moving out of the upper screen (which was located near the water table) became oxygenated and plugged the treatment zone. An additional problem with oxygen arose because of regionally-decreasing water table elevations in the area of the demonstration. This exposed a portion of the iron adjacent to the upper screen and, together with drawdown during pumping, led to a loss of permeability in the well in which water was extracted from the upper screen. These problems could have been avoided if the screened interval was below the water table, and if a packer had been placed in the well casing above the screen.

Tracer test data indicate that water re-circulated between the two Insitu treatment wells (ISTW) relatively quickly. Measurement of explosives concentrations in groundwater also showed that the performance of the ISTW met design expectations. The groundwater data also indicate that a year after installation of the ISTW, reactivity of the iron was still sufficiently high to reduce explosives concentrations to below detection limits.

An inherent disadvantage of the design used at Cornhusker Army Ammunition Plant (CAAP) was that the iron could not be readily replaced. In retrospect, if the reactive material would have been emplaced as a removable "cartridge" within a large dual-screen well, it would have provided an opportunity to remedy the plugging issue, however, plugging of injection screens is inherently a problem with circulation wells, and it is difficult to say with confidence if the well design improvements discussed here would represent a long-term solution.

Cost Analysis

The cost of each of the two ISTW was approximately $40,000. It is likely that modifications to the design would increase the cost per well. However, if the technology were implemented at a full scale in a similar setting, we believe that the cost per well would be similar to well costs for this demonstration.

1. INTRODUCTION

This final technical report documents the demonstration of a ZVI in situ treatment well (ISTW) to remove explosives from groundwater. The general purpose of the demonstration was to evaluate the efficacy of ZVI ISTW for treating explosives-contaminated groundwater.

1.1 Background

Groundwater contamination related to the explosives 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) represents a significant and widespread problem at U.S. Department of Defense (DoD) facilities. Current remediation approaches for TNT- and RDX-impacted groundwater typically involve groundwater extraction & treatment (pump & treat) with treatment by carbon adsorption or UV oxidation systems, both of which are costly to install and have short life cycles (e.g., 15 year re-capitalization periods). Furthermore, because of the chemical characteristics of RDX and in particular the sorptive properties of TNT, many of these pump & treat systems are projected to operate for decades, representing significant operation and maintenance (O&M) expenses. As an example, annual O&M costs associated with pump & treat remediation of groundwater impacted by TNT, related nitroaromatics and RDX at the Milan Army Ammunition Plant in Tennessee were estimated to be in the range of $1.4M per year (U.S. EPA, 1992) and at the Cornhusker Army Ammunition Plant (CAAP, U.S. EPA, 1994) approximately $1.2M per year.

Recent research has shown that TNT and RDX can be rapidly degraded using ZVI, and that the use of *in situ* PRB has very good potential for reducing the costs associated with groundwater cleanup at TNT- and RDX-impacted sites (Tratnyek et al., 2001, Oh et al., 2001; Johnson et al., 2007a,b). As an added benefit, ZVI can also treat a variety of contaminants (e.g., chlorinated solvents, chromate) that may co-occur in groundwater at RDX- and TNT-impacted sites. However, ZVI PRB are generally applicable in unconsolidated media and at depths of less than 70 feet below ground surface (bgs). To expand the applicability of ZVI to a broader range of settings, the injection of fine-grained ZVI into the subsurface has been proposed. An alternate approach, evaluated at the CAAP site, involves installation of a pair of dual-screened wells in which the conventional filter pack around the well screens has been replaced with coarse granular iron. Water moving into or out of the well screens passes through the ZVI and explosives are removed. The rate of explosives reaction with ZVI is sufficiently fast that good capture of groundwater by the wells can be achieved.

1.2 Objectives of the Demonstration

The objectives of this technology demonstration are:

1. Demonstrate that TNT and RDX can be degraded in situ to acceptable levels (i.e., the MDL) using a ZVI ISTW.

2. Evaluate ISTW well pair hydraulics.

3. Identify design and operational factors that influence successful implementation and continued operation of the ZVI ISTW approach.

The in situ treatment well system described in this final report was conducted at Load Line 2 at the Cornhusker Army Ammunitions Plant (CAAP) in Grand Island, Nebraska ("the site"). The advantages of the ZVI ISTW technology are that it can be installed at any depth and in any material in which large-diameter wells can be installed. Because groundwater remains below the surface during treatment, pumping costs can be minimized and there is no net removal of groundwater.

1.3 Stakeholder/End-User Issues

The demonstration showed that under field conditions explosives concentrations could be reduced below 1 μg/L. However, the particular design used in this demonstration proved susceptible to plugging over time, and as a result, subsequent engineering design will be necessary before the technology is ready for full-scale implementation.

2. TECHNOLOGY DESCRIPTION

ZVI ISTW are conceptually simple *in situ* remediation systems that involve emplacement of iron filings/shavings in the annular space around a pair (or more) of dual-screened wells. The two screens each well are separated from one another by a packer inside of the well and by bentonite grout outside the well. In each well, water is extracted from one of the screens using a submersible pump and injected into the other screen. The depth intervals in which injection and extraction occur are inverted in adjacent wells to create a circulation cell between screens in the adjacent wells. This approach is generally more robust, and produces a better capture zone, than trying to induce vertical flow between screens on an individual well (Johnson and Simon, 2007).

Recent laboratory studies funded by Strategic Environmental Research and Development Program (SERDP) have demonstrated that ZVI can rapidly degrade TNT and RDX. For TNT, Tratnyek et al (2001) showed that essentially all of the degradation products become completely sequestered on the iron, a process which can be sustained for thousands of pore volumes, even at very high flow rates and contaminant loadings. Similar performance is expected in the field, although site-specific geochemical conditions may have some impact on both performance and longevity. While laboratory data indicate that reduction of RDX by iron is rapid, the fate of the degradation products is not as well understood and may not be as effective as for TNT. The RDX research (Oh et al., 2001) does however indicate that the performance of the ZVI is significantly enhanced when iron-reducing bacteria are present, and therefore a combined ZVI-bioremediation approach may be most suitable to treat RDX.

Based on the available laboratory TNT and RDX degradation data, residence times of a few minutes are all that are required to reduce explosives levels to low levels. At the same time, the paired recirculation well approach necessitates much slower pumping rates than for conventional pump and treat (P&T, so adequate residence times can be achieved with wells of modest diameter) e.g., in this study, 18 inch diameter boreholes were installed using conventional water supply well drilling equipment, and as a result mobilization and installation costs were not prohibitively high).

2.1 Technology Development and Application

Groundwater circulation wells are a commonly used remediation technology for both the delivery of materials to the subsurface and for the removal of contaminants using an in situ treatment (e.g., in well air stripping). The main technical risks associated with this technology relate to the potential influence of site-specific geochemical conditions on: 1) RDX and TNT reactivity in the ZVI, 2) completeness of removal of the primary contaminants and degradation products, and 3) long-term ISTW performance. Several recent SERDP funded projects evaluated the fate of TNT and RDX degradation with ZVI in laboratory and ex situ columns under different geochemical conditions (SERDP ER-1231 and ER-1232). The site-specific pre-design optimization studies discussed below (including ex situ ZVI columns and detailed geochemical analyses) also address this uncertainty.

2.2 Previous Testing of the Technology

As mentioned above, ZVI is being used at a growing number of sites to treat a range of contaminants, including chlorinated solvents, chromium and nitrate. In the context of explosives, to date most testing has been in the laboratory or in ex situ columns. TNT and RDX behavior have been examined in laboratory batch and column experiments, including ZVI-filled ex situ columns at the Umatilla Chemical Storage Depot in Umatilla, Oregon. The conclusions of that work can be summarized as follows:

a. Degradation of both RDX and TNT on ZVI is rapid, with half lives measured in seconds to minutes.

b. Over time, reactivity of the ZVI decreases due to passivation, but half lives are still on the order of minutes for TNT and RDX.

c. In the ex situ field tests and Umatilla, dissolved oxygen (DO) present in the groundwater appears to be the primary contributor to passivation of the ZVI.

d. Oxygen was also the primary contributor to plugging of the columns by precipitated iron oxides.

e. Plugging of the ZVI in the presence of oxygen can be minimized by using fairly coarse (8/18 mesh) iron and iron/sand mixtures.

f. TNT is quantitatively reduced to triaminotoluene (TAT) by the ZVI.

g. The TAT is unstable in the presence of oxygen. Experiments with 13C-labeled TAT show that all of the radioactivity associated with TAT disappears from solution within 2-3 days, indicating that it is quantitatively precipitated. We believe this occurs in part through polymerization.

2.3 Factors Affecting Cost and Performance

A number of factors affect the cost and performance of technology in field applications. The key factors are:

1. **The concentration and distribution of explosives** in the groundwater to be treated will impact the costs and performance. Higher concentrations of explosives will require longer residence times in the ISTW. This is not expected to be a major issue at most sites.
2. **The chemistry of the aquifer** to be treated will impact the cost and performance. The primary issues of concern will be the presence of dissolved oxygen, carbonate, nitrate, sulfate, or other species that may passivate the surface of the iron or plug the ISTW.
3. **The depth to groundwater** will impact the cost of well installation.

4. **The groundwater velocity** in the aquifer will impact the design of the ISTW (e.g., pumping rate needed to ensure capture).
5. **Geological heterogeneities** in the aquifer.
6. **Seasonal variation in groundwater flow direction** will impact the design of the ISTW primarily by requiring increased lateral extent of the treatment zone needed to ensure capture of the plume.

2.4 Advantages and Limitations

Prominent alternative technologies to in situ ZVI ISTW for explosives-impacted groundwater are: 1) groundwater pump and treat followed by ex situ degradation; and 2) groundwater pump and treat followed by adsorption on carbon.

Current approaches for the remediation of explosives-impacted groundwater typically involve long-term pump and treat solutions involving capital-intensive ex situ treatment components (ex situ bioreactors or ion exchange systems) and long-term O&M costs. As an example, annual O&M costs associated with pump & treat remediation of groundwater impacted by TNT, related nitroaromatics and RDX at the CAAP (U.S. EPA, 1994) approximately $1.2M per year. At many sites the initial capital costs for ISTW wells are expected to be similar to those for pump and treat with carbon sorption. However, the O&M costs for the ISTW are expected to be lower.

The main advantages of the remediation technology are:

- Lower capital and O&M costs than alternative technologies which involve groundwater, pump and treat with high O&M costs;
- Contaminants are destroyed and not simply transferred to another medium; and
- Ability to treat possible co-contaminants such as nitrate, TCE or chromium.

The main limitations of the technology are:

- Insufficient longevity of the iron due to passivation and/or plugging; and
- Initial capital costs.

3. DEMONSTRATION DESIGN

This section presents the design of demonstration for remediation of explosives-impacted groundwater using the ZVI ISTW approach. Specific subsections present:

- Performance objectives of the technology demonstration (Section 3.1)
- A description of the criteria and requirements used in site selection (Section 3.2)
- A summary of the available site history and site characterization data (Section 3.3)
- A summary of ongoing operations at the demonstration site (Section 3.4)
- A detailed description of the pre-design activities to be performed as part of the technology demonstration (Section 3.5)

3.1 Performance Objectives

The performance objectives are provided in Table 3-1.

Table 3-1. Performance Objectives.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance
Qualitative	"Simple to operate"	Minimal effort to operate (i.e., semi-passive operation after installation)	Performance objective met
	Reduction in co-contaminants (RDX,TNT) downgradient of treatment zone	Reduce concentration of contaminants (RDX,TNT)	Performance objective met
Quantitative	Reduce explosives concentration down-gradient of treatment zone	> 90% reduction in concentration (or less than 1 ug/L)	Performance objective met

3.2 Selection of Test Site

The criteria and requirements used in selecting the test site for the passive ZVI ISTW demonstration were as follows:

1) Significant (i.e., > 100 µg/L) concentrations of TNT and/or RDX in groundwater so that it was be possible to demonstrate that the technology can reduce concentrations by >90%.

2) Interest on the part of the site manager to allow access to the site during the demonstration.

3) Shallow, permeable aquifer with a significant groundwater contamination plume.

3.3 Test Site History/Characteristics

The site identified for this demonstration is CAAP, located near Grand Island, Nebraska. Information on the test site history and characteristics is presented in the June 1998 Annual Sampling Event for the Long-Term Monitoring Program, CAAP, Grand Island, Nebraska, by Woodward-Clyde (Woodward-Clyde, 1999). The following sections of this Demonstration Plan present a summary of this information, with significant sections of text taken directly from that report.

3.3.1 Test Site History

CAAP is located in central Nebraska near Grand Island. The CAAP occupies nearly 12,000 acres as shown in Figure 3-1. Figure 3-2 shows a map of the Load Line 2 area at the CAAP. The locations of the former ponds used for the demonstration are shown on the map.

Figure 3-1. Map of Cornhusker Army Ammunition Plant.

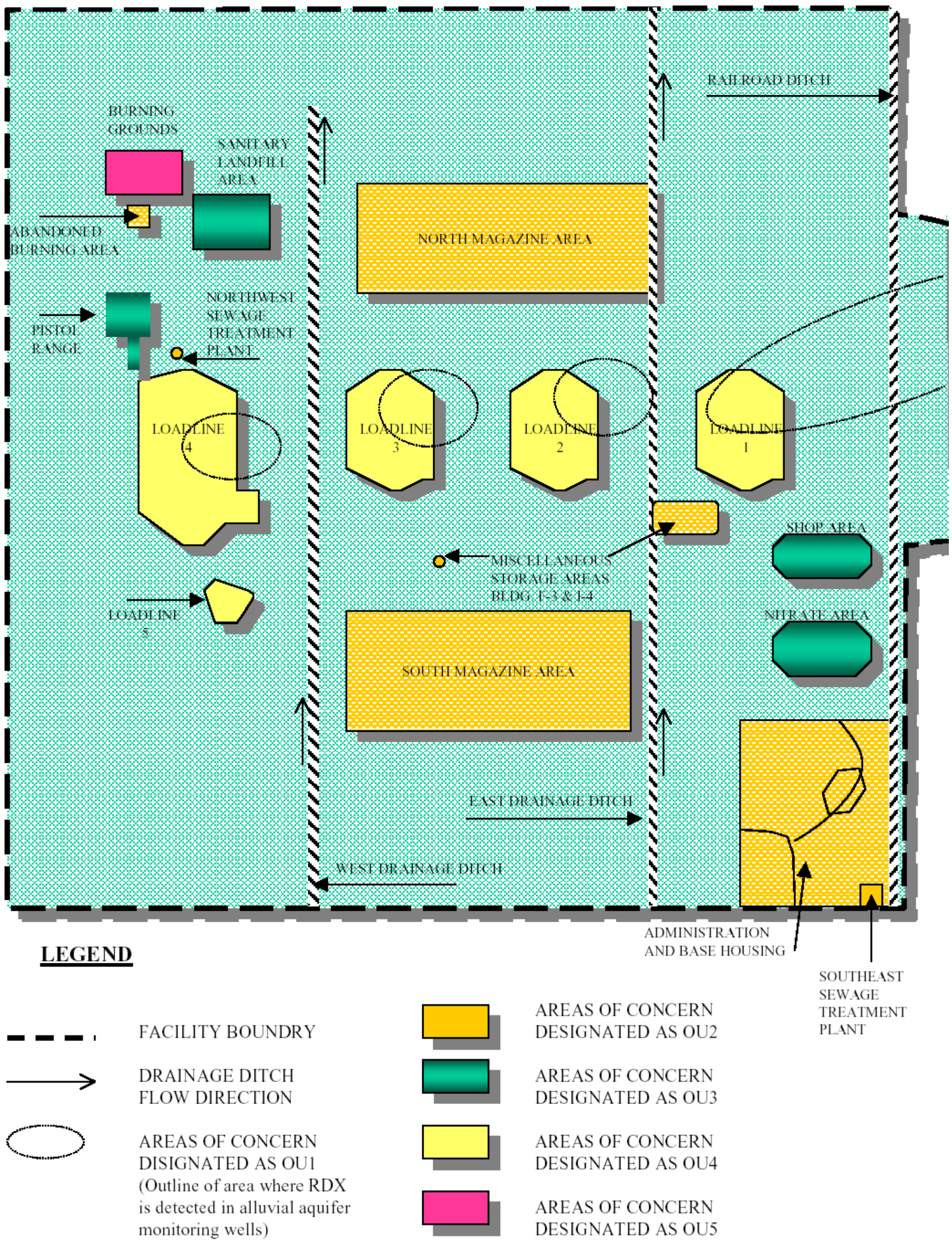
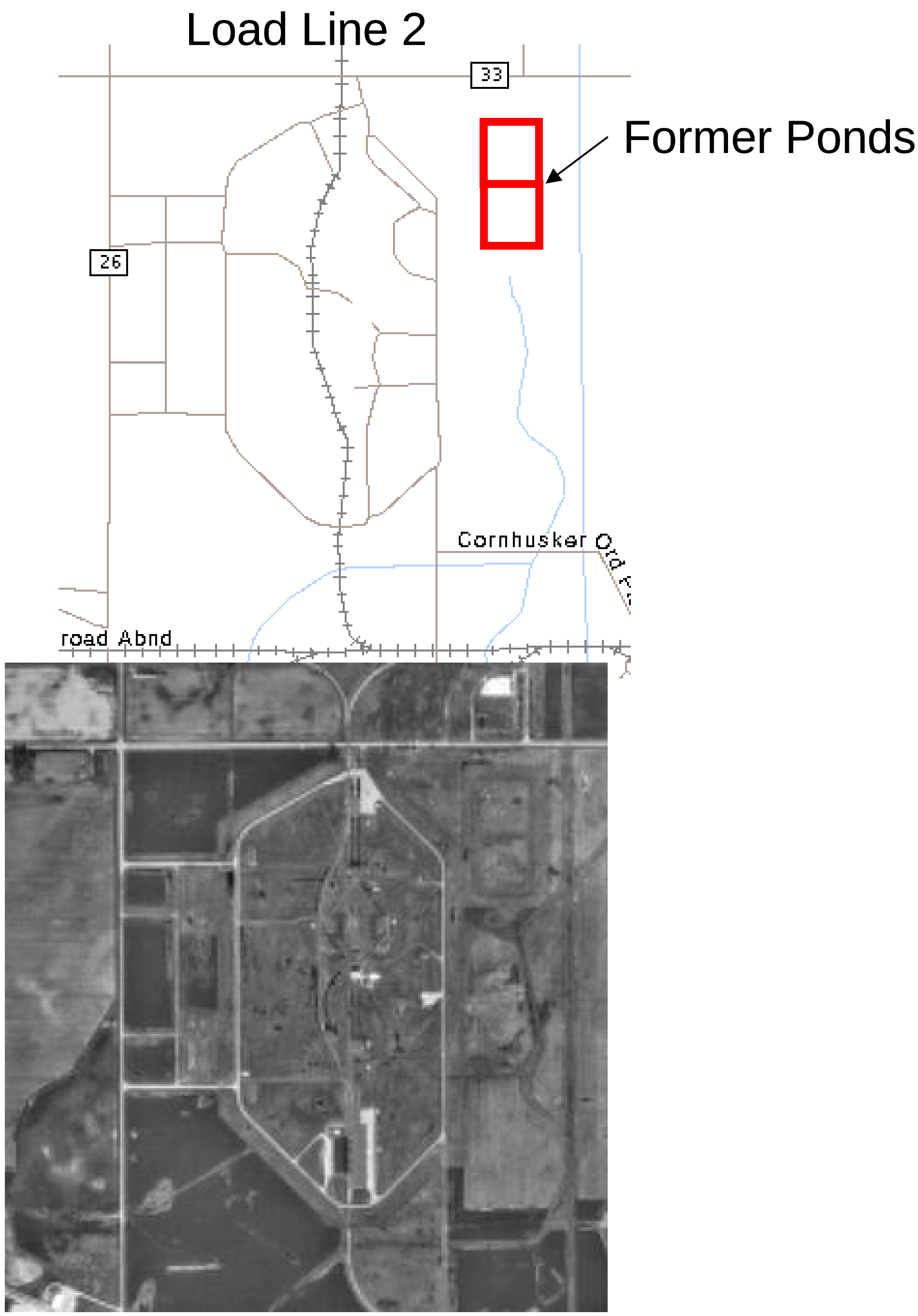


Figure 3-2. Map of Load Line 2, CAAP.



CAAP was constructed and became fully operational in 1942 as a U.S. Government-owned, contractor-operated facility. CAAP was responsible for the production of artillery shells, mines, bombs, and rockets for World War II and the Korean and Vietnam conflicts. The plant was operated intermittently for 30 years with the most recent operations ending in 1973. From 1942-1945, various bombs, shells, boosters and supplementary charges were produced at CAAP using primarily TNT. From 1950-1955, artillery shells and rockets were produced using a mixture of TNT, cyclonite RDX, and cyclotetramethylenetetranitramine (HMX).

CAAP was activated again from 1965-1973 to produce bombs, projectiles, and gravel mini-mines. Explosive wastes and residues associated with munitions loading, assembly, and packing operations have resulted in a groundwater contamination plume that originates at waste leach pits and cesspools of the CAAP load lines and extends east-northeastward into the city of Grand Island, Nebraska.

3.3.2 Environmental Setting, Geology and Hydrology

The general geologic description summarized here was interpreted from soil boring logs completed during the installation of on- and off-post monitoring wells (WJE 1993), as well as regional data from the Soil Survey for Hall County (USDA 1962). In general, the geologic units underlying the CAAP study area include (in descending order from the surface) the following:

> Alluvial silty clay and topsoil near the surface (from about 0 to 5 feet in depth)
>
> Alluvial sands and gravels of the Grand Island Formation (about 50 to 60 feet in thickness)
>
> A low-permeability, alluvial silty clay unit of the Fullerton Formation (about 5 to 15 feet in thickness). This has also been referred to as the blue clay unit in previous reports (WJE 1993).
>
> Alluvial sands and gravels of the Holdrege Formation (reported to be up to 200 feet in thickness)

These geologic units are laterally extensive across the CAAP facility and the northwestern part of the city of Grand Island. The deepest monitoring well borings (off post) extend 10 to 20 feet below the Fullerton clay unit into the Holdrege Formation.

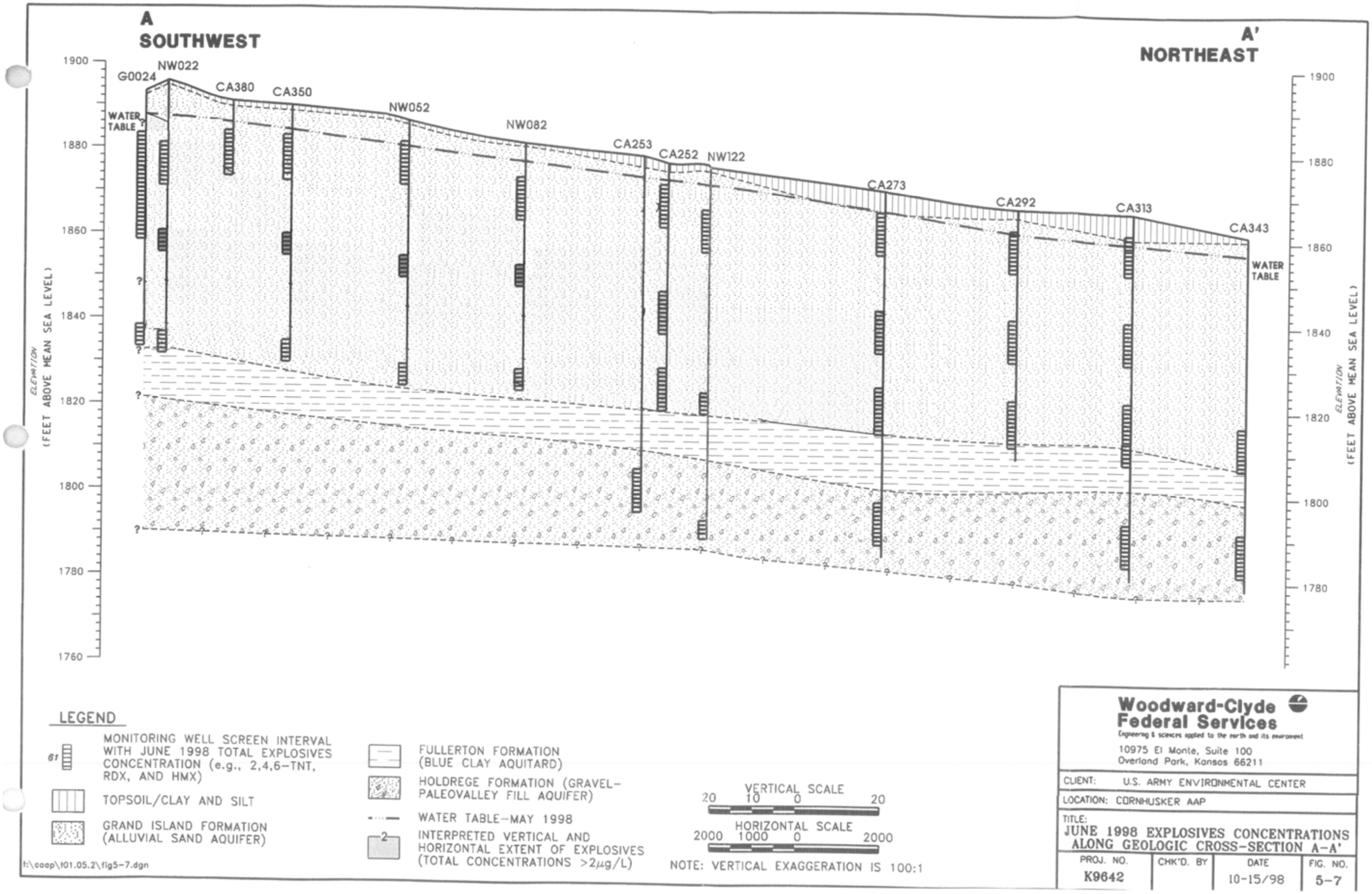


Figure 3-3. Geologic Cross Section.

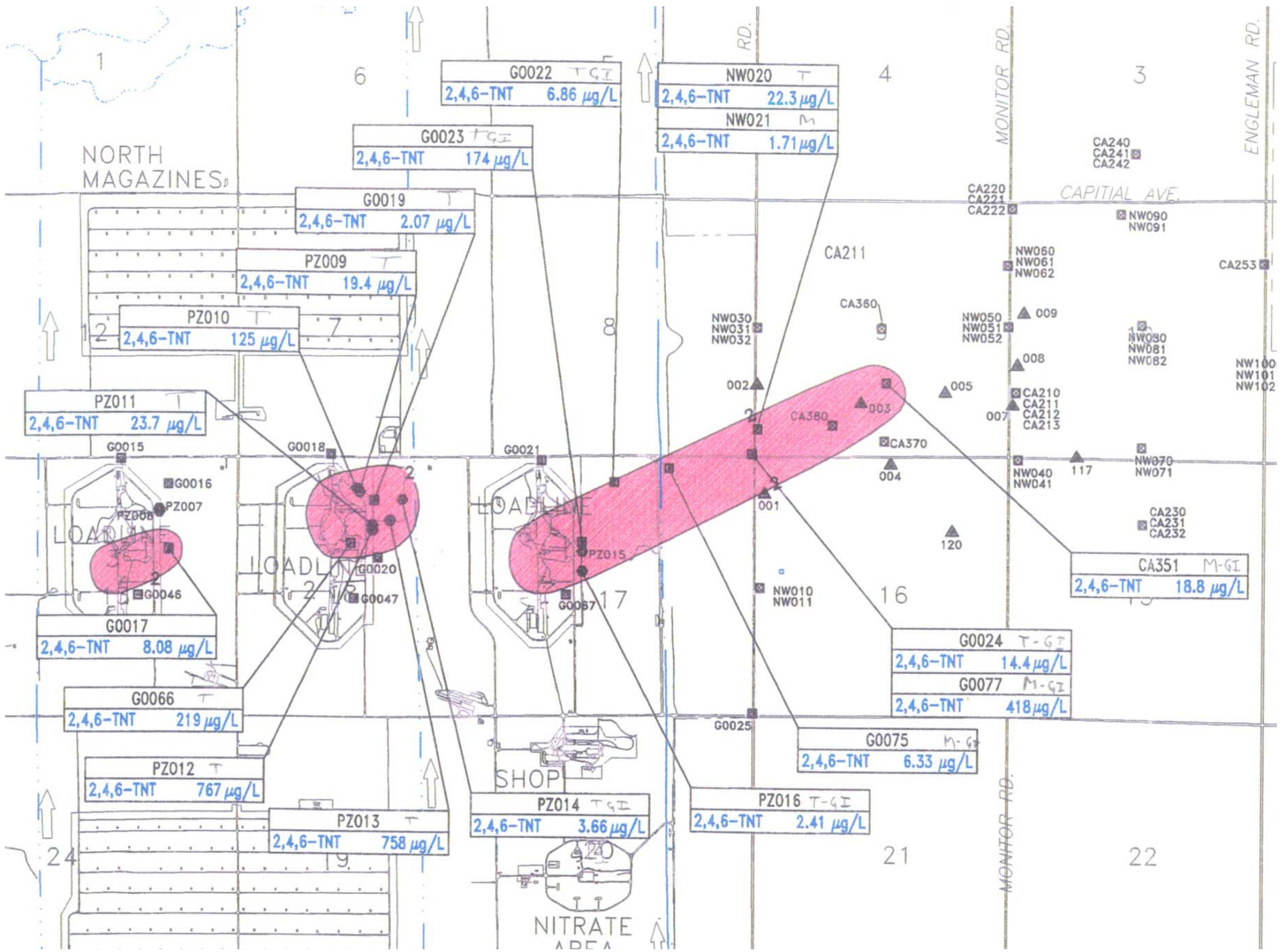


Figure 3-4. Site Plan View Showing the TNT Plumes From Load Lines 1, 2 and 3 at CAAP.

Shallow groundwater underlying the facility occurs as an unconfined water table aquifer within the alluvial sands and gravels of the Grand Island Formation. The water table surface is generally less than 10 feet below the ground surface. Total thickness of the water table aquifer ranges from about 50 to 60 feet within the study area. Hydraulic conductivity values range up to 670 feet per day. The predominant groundwater flow direction within the water table aquifer near the CAAP facility is to the northeast towards the city of Grand Island. Regional horizontal gradients of about 0.001 have been measured in the area.

The Grand Island Formation aquifer is used regionally as a water supply source for irrigation and potable water. Locally, there are a number of irrigation wells in use east of the facility; however, all private domestic water is being supplied by the City of Grand Island. The city's municipal well field is located southeast of the city near the Platte River (about 10 miles southeast of CAAP).

The underlying clay is a relatively low-permeability unit that appears to act as a barrier to groundwater flow (i.e., aquitard) in the CAAP study area (Woodward-Clyde, 1999). Justification for this interpretation includes:

The presence of head differences across the Fullerton clay unit as measured between the Grand Island Formation aquifer and the underlying Holdrege Formation aquifer.

The absence of contamination below the Fullerton clay unit at locations where contamination is present at the base of the Grand Island Formation aquifer

The sands and gravels of the Holdrege Formation act as a confined aquifer unit (confined by the overlying Fullerton clay unit) in the CAAP study area. Based on water level data from the deep monitoring wells, the general groundwater flow direction in the Holdrege Formation appears to have a northeasterly component (similar to the overlying Grand Island Formation aquifer).

3.3.3 Contaminant Distribution within the Pilot Test Area

The off-post explosives plume originates on the northeast edge of the CAAP Facility (near Load Line 1) and extends over 21,000 feet northeast into the surroundings rural and urban areas. The axis of the off-post explosives plume trends from southwest to northeast (Figure 3-4). The highest explosives concentrations were located near the facility boundary. Explosives concentrations declined to the northeast. The plume was detected at depths of 6 to 57 feet bgs and approximately 5 to 33 feet below the water table. There appears to be a clean zone near the water table in the distal edges of the plume. Explosives were not detected in the deep aquifer (Holdrege Formation). The Fullerton Formation appears to act as a natural barrier, retarding the vertical migration of explosives to the underlying Holdrege Formation (gravel-paleovalley fill aquifer).

3.4 Present Operations

Current operations at CAAP consist of a groundwater extraction and treatment system. No other operations were conducted in the vicinity of Load Line 2.

3.5 Testing and Evaluation Plan

The demonstration was conducted in four phases of work. The first phase consisted of site characterization and engineering design (Phase 1). This was followed by installation of the ZVI ISTW (Phase 2). Phase 3 was performance monitoring of the ZVI ISTW. Phase 4 was numerical modeling of ISTW hydraulic and degradation performance. The timeline for the demonstration is shown in Table 3-3.

Table 3-2. Project Timeline.

		2003												2004												2005						
Phase	Activity	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J
1a	Site characterization																															
1b	Final ISTW design																															
2	ISTW installation																															
3	Performance monitroing																															
4	Numerical modeling																															

3.6 Characterization & Engineering Design (Phase 1)

Following approval of the demonstration plan, the project team conducted a series of pre-design and design activities at the site. These included on-site ZVI reactivity testing using site groundwater and ex situ columns; site characterization, including hydraulic testing, detailed contaminant distribution measurements; assessment of groundwater geochemistry, preliminary numerical modeling and engineering design for ISTW installation.

3.6.1 Groundwater Chemical Analysis

Groundwater samples were collected and analyzed to determine explosives concentrations and the general characteristics of the groundwater. Analyses included:

- Field parameters (DO, ORP, pH, conductivity, alkalinity and temperature);
- TNT, RDX;
- Selected anions (nitrate and sulfate); and
- Cations (sodium, potassium, magnesium, calcium).

Samples were collected by OHSU personnel following standard sampling protocols. Field parameters were analyzed in on site. TNT and RDX samples were extracted on site using Waters “Sep-Paks” and were analyzed at OHSU. Anions and cations were analyzed at OHSU and Columbia Analytical Laboratory, Inc. by ion chromatography and wet chemical methods.

Table 3-2 summarizes the parameters that were analyzed as part of the pre-demonstration characterization, and provides details of analytical methods, container size and type, preservation method, and sample holding times.

Table 3-3. Analytical Parameters.

Parameter	Sample Collection Volume	Field Preservation	Analysis Location	Sample Holding Time
TNT/RDX	1 liter	Sep-Pak	OHSU	2 weeks
Anions	40 mL	none	OHSU	2 weeks
Cations	40 mL	none	OHSU	2 weeks
Dissolved Oxygen	In line meter	none	Field	none
Field Parameters (pH,temp,conductance, Eh)	In line meter	none	field	none
Ferrous iron	10 mL	none	Field	none
Alkalinity	25 mL	none	field	none

3.6.2 Field Ex Situ Column Testing

A field ex situ column study was performed to gather data to assess the long-term performance of the ZVI ISTW at the site. The objectives of the study are:

Evaluate if plugging limited the lifetime of the ZVI ISTW; and

Evaluate if passivation of the iron by precipitation limited the reactivity of the ZVI.

ZVI has been shown in the laboratory to become plugged when exposed to oxygenated groundwater (Johnson et al., 2005). Data from CAAP indicate that DO levels at the site are ~1 mg/L. Based on current laboratory experiments, plugging issues in the barrier could be avoided but our intent was to use ex situ columns to assess plugging under site conditions. Unfortunately, as we observed at the Umatilla Depot, DO levels in the pumped groundwater were significantly above ambient groundwater levels. As a consequence, plugging occurred within a matter of a few days and longer-term studies could not be conducted.

3.6.3 Mini Pumping Tests

Prior to installation of the ISTW, a series of pumping tests were conducted to determine the appropriate depth intervals for the well screens. These tests were conducted in June 2004 and followed the procedure developed by Cho et al. (2000) in which the rate at which water can be pumped from a will under conditions of steady-state drawdown is used to determine hydraulic conductivity. In the case of these tests, a 30 cm long well screen (~4 cm OD) was used and a 30 cm drawdown was established for each test. The time required to pump one liter of water from the well was used to determine K.

Data from four vertical profiles were collected (Figure 3.5). They showed a general pattern of layered hydraulic conductivity values on ~1.5m intervals (Figure 3.6). Beginning at the water table and moving down, the average K values for those layers were 15, 3, 9 and 3 m/d, respectively. As a consequence, the screened intervals for the wells were placed in the the higher-K intervals at 5.8-7.3 and 9.1-10.6 meters bgs.

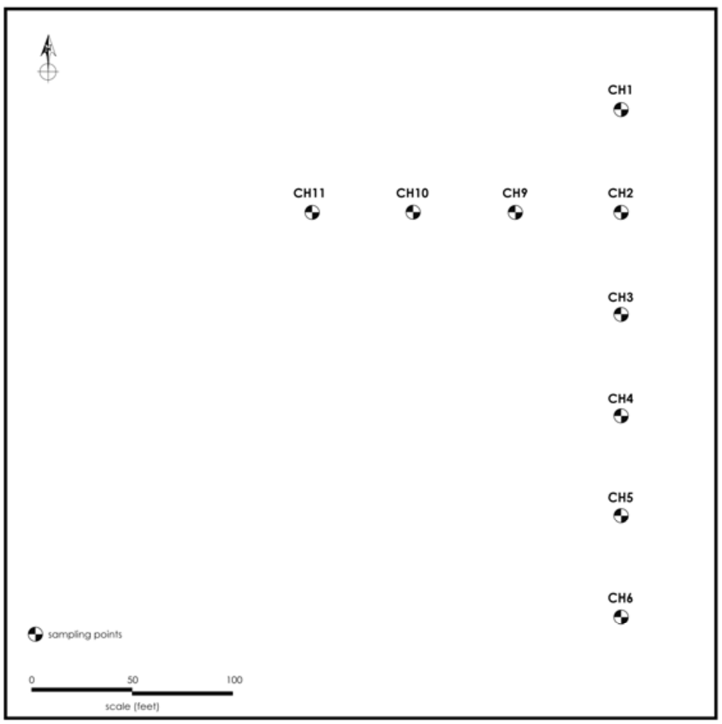


Figure 3-5. Site Plan View Showing Locations of the Pre-installation Sampling Locations.

Figure 3-6. Plan View Showing Locations for the Four ISTW Vertical Profiles for the Mini Pumping Tests.

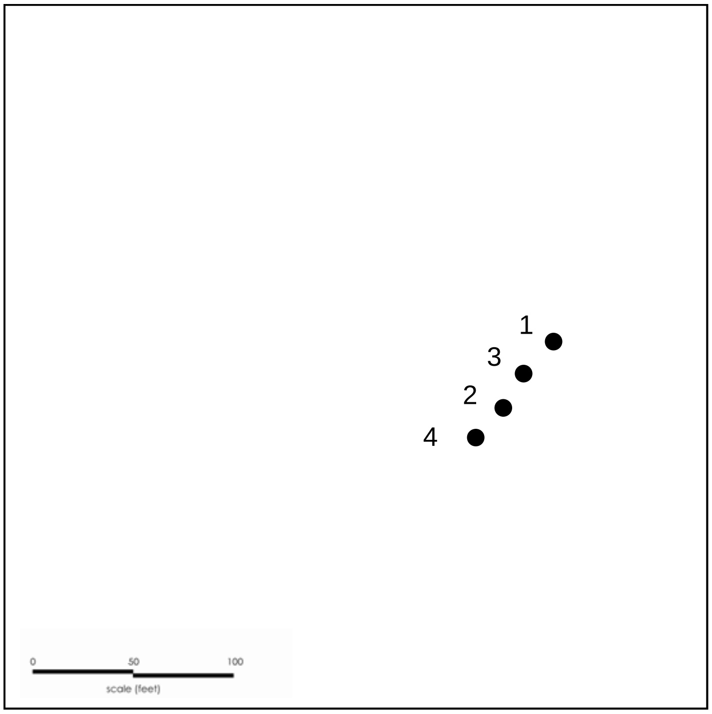


Table 3-4. Hydraulic Conductivity (K) Profiles Determined Using Mini-pump Tests. (Yellow indicates K values higher than 3 m/d).

Depth (m bgs)	Hydraulic conductivity (m/d)			
	4	2	3	1
5.5-5.8	6.5	33.9	18.5	25.8
5.8-6.1	23.8	3.4	12.7	27.8
6.1-6.4	12.7	4.3	10.3	7.9
6.4-6.7	13.3	8.9	8.7	28.2
6.7-7.0	6.5	16.8	6.8	16.4
7.0-7.3	9.6	21.9	8.0	24.4
7.3-7.6	0.9	0.8	2.5	1.2
7.6-7.9	2.0	5.0	0.9	2.1
7.9-8.2	0.8	6.9	1.7	1.1
8.2-8.5	2.3	8.8	0.6	3.2
8.5-8.8	1.3	0.7	1.7	1.3
8.8-9.1	1.3	51.6	0.5	17.4
9.1-9.4	12.0	0.8	11.6	3.4
9.4-9.7	3.2	4.6	54.9	1.4
9.7-10.0	7.2	4.1	4.8	2.9
10.0-10.3	5.1	3.3	3.6	14.6
10.3-10.6	3.0	1.1	9.6	2.4
10.6-10.9	2.9	1.0	1.1	1.5
10.9-11.2	0.7	1.1	0.1	0.4
11.2-11.5	15.8	1.7	2.3	1.1
11.5-11.8	3.9	3.2	1.1	49.3
11.8-12.1	3.2	1.2	7.4	3.9
12.1-12.4	0.9	5.7	4.2	10.4

3.6.4 Numerical Flow and Transport Modeling

Using the characterization data described above, a preliminary three-dimensional numerical groundwater flow and transport model was developed for the ISTW and surrounding aquifer. MODFLOW/MODPATH was used to model flow and conservative transport.

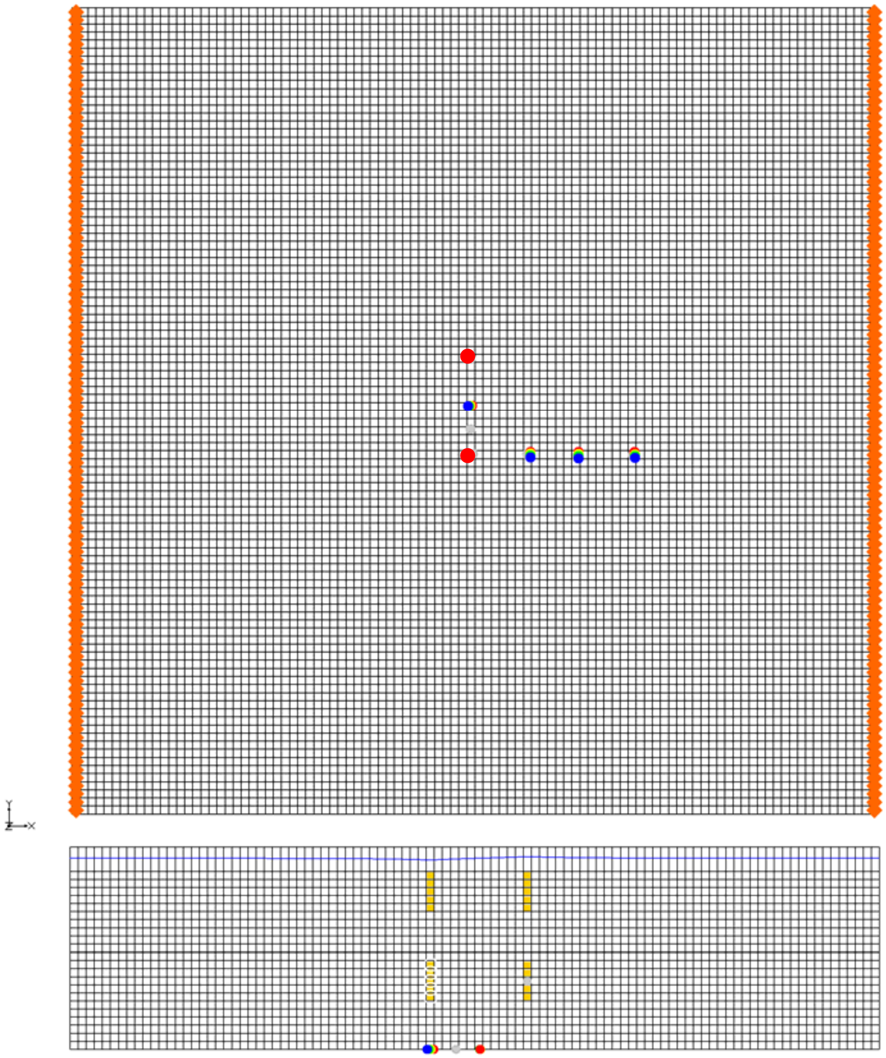


Figure 3-7. Plan and Cross-section Views of the Numerical Model Grid.

For these simulations water was extracted from one of the lower well screens and injected into the upper screen of that well, while water was injected into the upper screen of the other well and extracted from the lower screen of that well. The flow through each well screen was maintained at ~4 liters per minute (6000 liters per day). A total porosity of 0.3 was assumed for the simulation. The data in Figure 3.8a show the general flow pathway for particles injected at deep injection screen. Approximately 90% of the injected particles are captured by one of the two extraction screens (i.e., 90% recirculation). The model also indicates that a ~12m wide swath of water entering the up-gradient edge of the domain over its entire 7.5 m thickness is captured by the ISTW system.

Figure 3.9 shows the numerical simulation of water level changes during startup and shut-down of the ISTW system based on the simulation described above.

a)

b)

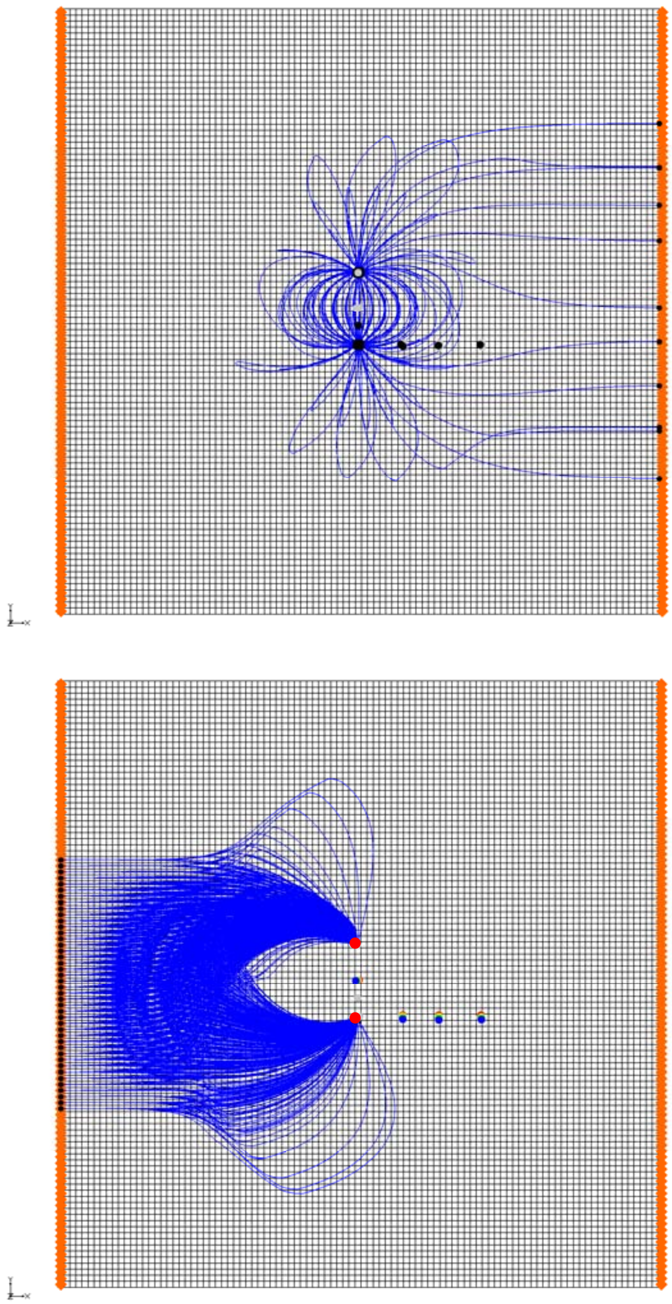


Figure 3-8. MODPATH Particle Tracks for: a) Water injected at one of the lower ISTW screens; and b) particles coming from up-gradient of the ISTW.

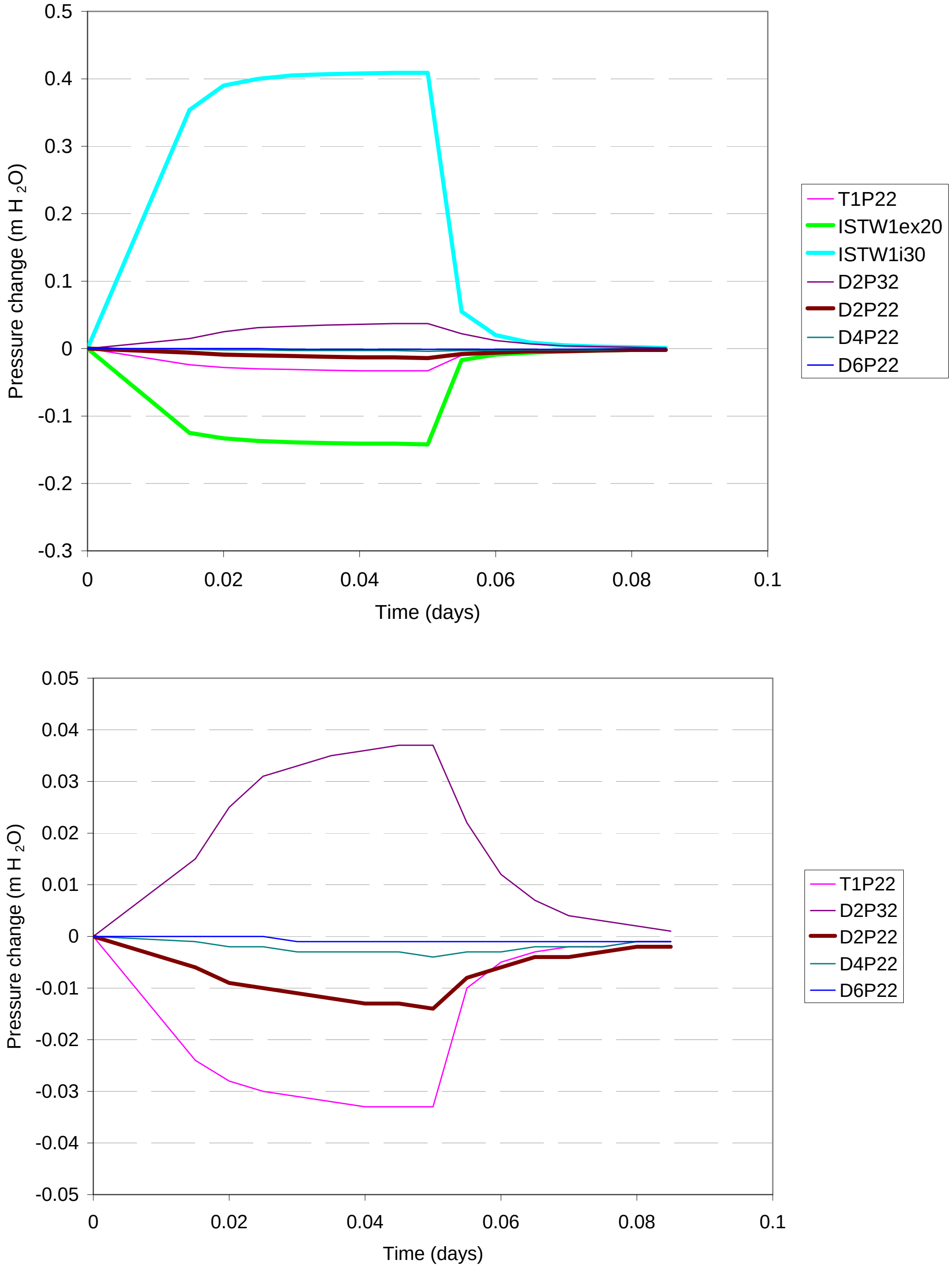
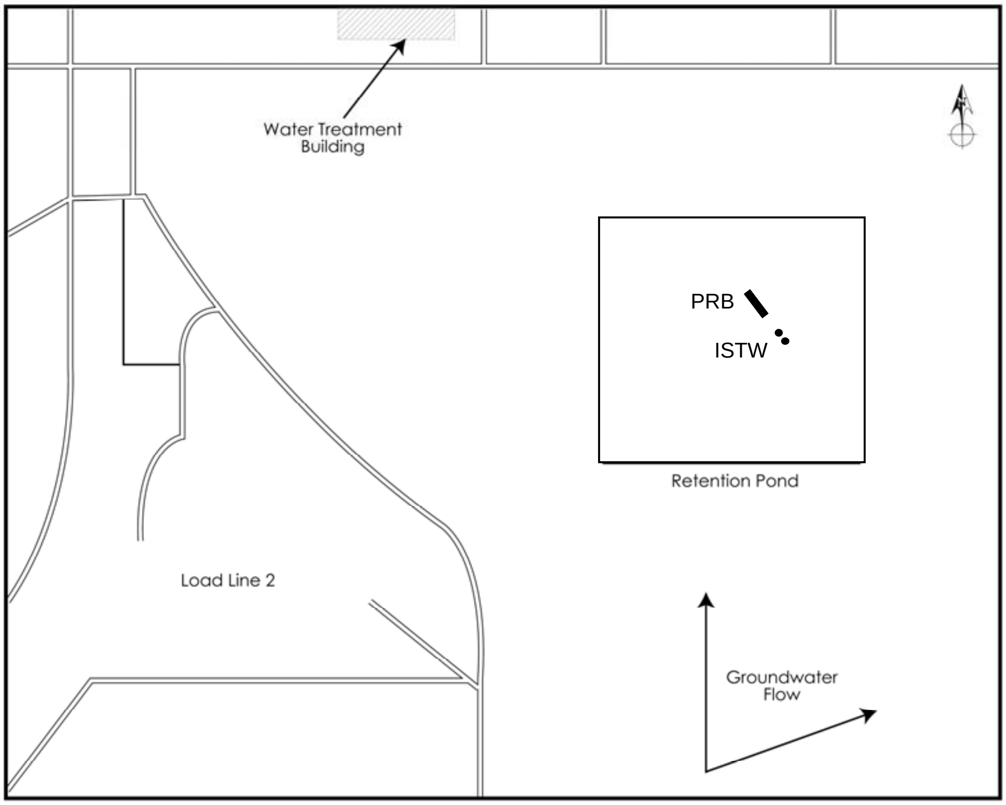


Figure 3-9. Numerical Model Results for Pumping From a Single ISTW at 4 Liters per Minute.

4. INSTALLATION OF THE ZVI ISTW (PHASE 2)

Installation of the ZIV ISTW is described briefly here. The “as built” location and design are shown in Figures 4-1 to 4-3.

Figure 4-1. Site Map Showing "as built" Location of the ZVI ISTW.



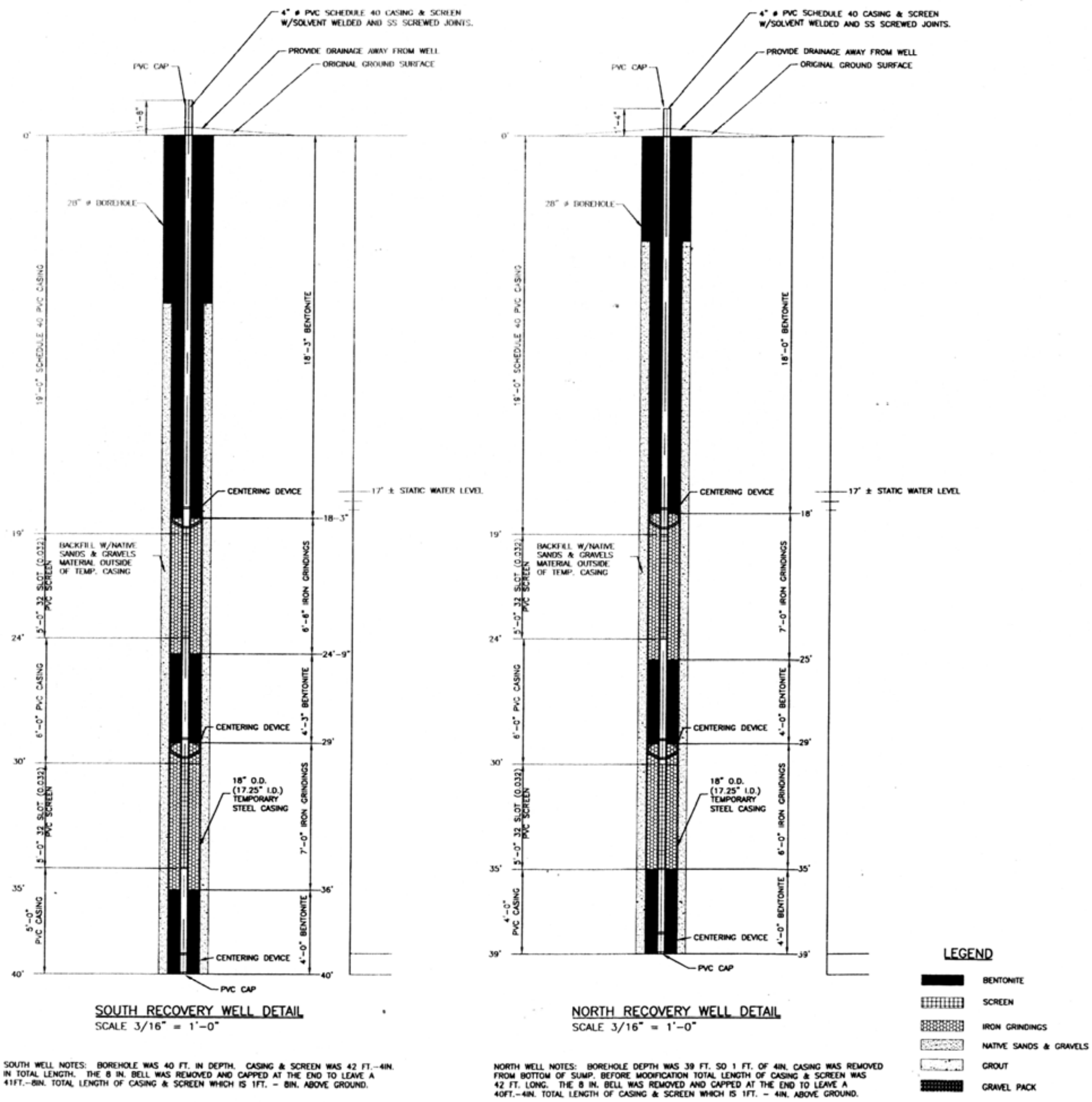


Figure 4-2. Cross-section Drawing of the "as built" ZVI ISTW.

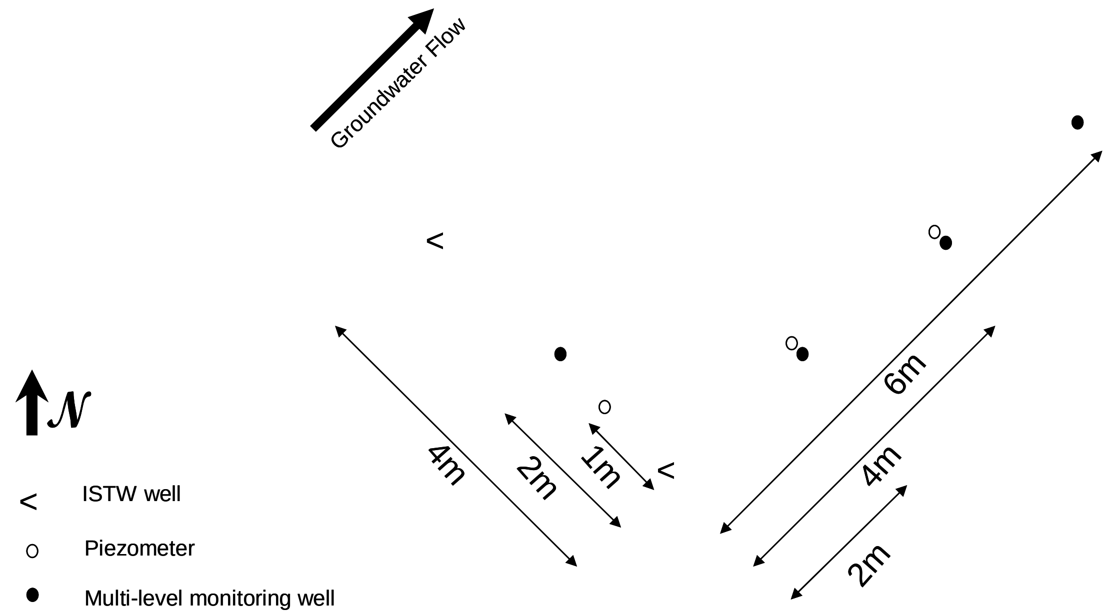


Figure 4-3. Plan View Drawing of the "as built" ZVI ISTW Showing Locations of the Monitoring Points.

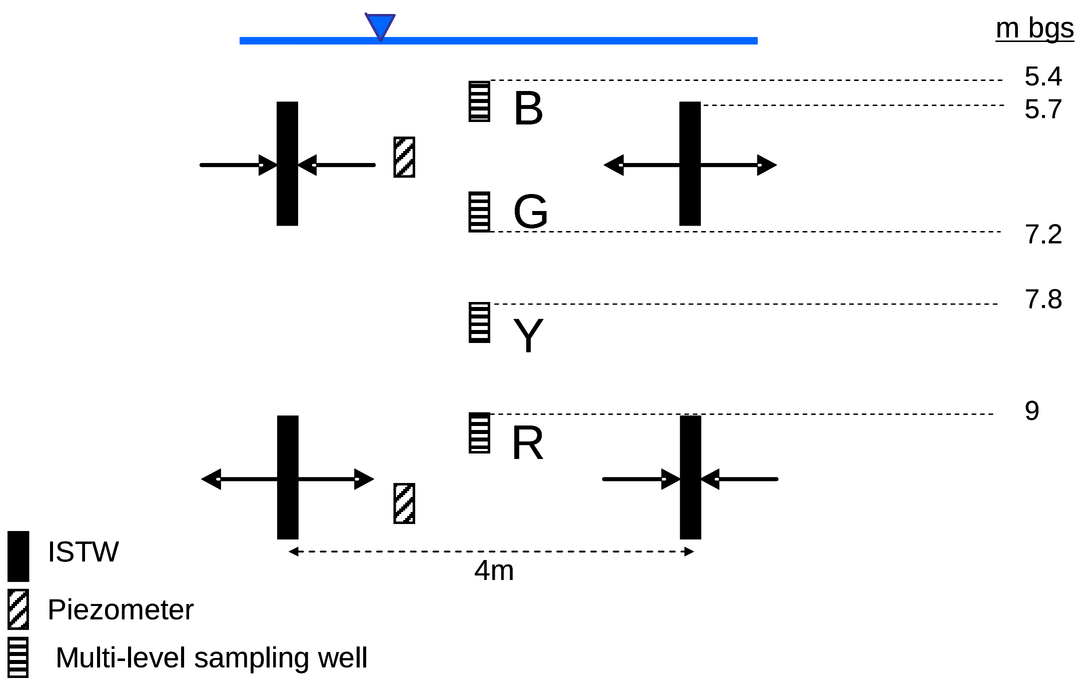


Figure 4-4. Section View Drawing Showing the Screened Intervals of the ZVI ISTW Piezometers and Multi-level Monitoring Wells.

4.1.1 Residuals Handling

All fluids generated during well purging and equipment cleaning remained on-site. During emplacement of the ISTW, both clean and contaminated soils were removed from the subsurface. The soils overlying the aquifer were clean. These soils were segregated from any contaminated soils. Soils from below the seasonally-high water table were assumed contaminated. These were stored above ground for less than 1 day and were used in the emplacement of the ZVI ISTW. Uncontaminated soils were spread on site.

4.1.2 Operating Parameters for the Technology

Because the ZVI ISTW technology is entirely in situ, the operating parameters critical to its performance involve the reactivity of the iron and the hydraulic conductivity of the iron. The primary indicators of operation of the ISTW are:

1. Explosives concentrations up- and down-gradient of the barrier; and
2. Flow of water through the ISTW.

4.1.3 Experimental Design

The contaminated fluid to be treated by the ZVI ISTW remediation technology consisted of the groundwater that flows into the treatment zone created by the ISTW. The treated water stream consists of the groundwater downgradient of the groundwater treatment zone. Groundwater monitoring was conducted to confirm that the performance of the ZVI ISTW technology was achieving the target objectives. Details of the technology validation approach are presented in Section 4.2. This approach demonstrated that the ZVI ISTW reduced explosives concentrations at the down gradient performance monitoring wells.

4.1.4 Sampling Plan

The effectiveness of the ZVI ISTW was determined using the results of the groundwater sampling and analysis conducted in performance monitoring wells. Samples were collected from the groundwater monitoring wells and analyzed in the field or in the laboratory depending on the specific parameter being measured.

The experimental controls incorporated in the design of the demonstration ensured that the monitoring data provided an unequivocal and reliable assessment of the applicability of ZVI ISTW systems at DoD sites. The tracer tests provided the project team with an understanding of advective and dispersive transport processes in the test area.

4.1.5 Demobilization

Upon completion of the demonstration, all aboveground equipment and structures were removed. All subsurface devices were removed in accordance with CAAP policy.

4.1.6 Management and Staffing

The project management personnel for this project are presented in Figure 4-4. Rick Johnson (OHSU) was the Principal Investigator, with responsibility for the overall management, direction, and execution of the demonstration. Paul Tratnyek (OHSU) was the Technical Reviewer and provide review of project activities, engineering design and project strategy. R. Brad Thoms (OHSU) coordinated daily management of the project activities and acted as the Quality Assurance Officer for the demonstration.

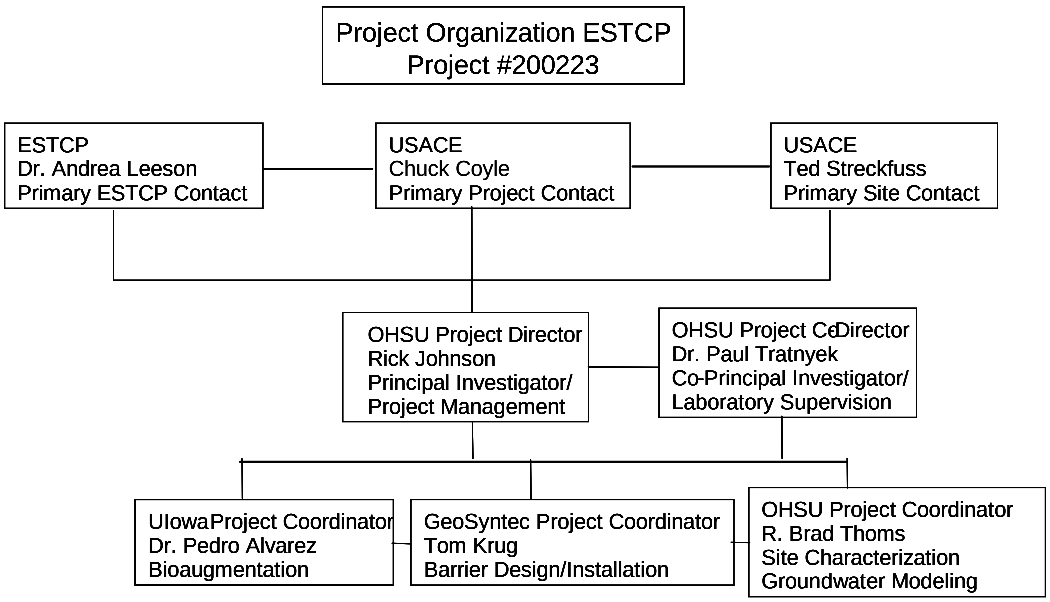


Figure 4-5. Project Organization for ESTCP ZVI ISTW Pilot Test.

5. PERFORMANCE ASSESSMENT

5.1 Performance Criteria

Performance of the demonstration has been evaluated using the general performance criteria provided in Table 5-1. Qualitative and quantitative criteria are classed as either primary or secondary performance assessment criteria, respectively.

The primary criteria constitute the performance objectives of the technology demonstration. As stated in Section 1.2, the general objective of the demonstration is to evaluate the performance of the ZVI ISTW to degrade explosives in groundwater. In general, the performance criteria are used to evaluate this objective by:

Determining the ability of the ZVI ISTW to degrade explosives over the period of demonstration (~12 months in this case).

Evaluating ISTW hydraulics.

Evaluating the difficulty in implementing this technology at the field scale.

5.2 Performance Confirmation Methods

The success of the technology demonstration has been evaluated using the performance expectations and confirmation methods presented in Table 5-1. Successful implementation of the technology demonstrated that the technology results in significant reduction in TNT and RDX concentrations over the duration of the demonstration.

Table 5-1. Project Performance Criteria.

	Performance Criteria	Performance Metric	Confirmation Method	Location	Sample Matrix	Measurement
Primary	Qualitative					
	Extent of degradation	Decreased TNT and RDX concentrations downgradient of the ISTW	TNT/RDX concentration	PTA[1]	groundwater	TNT/RDX
	Quantitative					
	Mass flux from ISTW treatment zone	Decreased mass flux of TNT and RDX coming from the zone captured by the ISTW	TNT/RDX concentration	PTA	groundwater	TNT/RDX
Secondary	Qualitative					
	ISTW hydraulics	Tracer test	Bromide analyses	PTA	groundwater	Anion analysis, bromide specific ion electrode
	ISTW hydraulics	Small water level changes will occur if ISTW hydraulics change	Water level measurements	PTA	groundwater	Water level tape

Performance monitoring and assessment were conducted for a period of about 12 months. Groundwater samples were collected from the various monitoring wells for analysis of the parameters listed in Table 3-2.

[1] Pilot Test Area

The data obtained from the demonstration were used to estimate the rate and extent of degradation of TNT and RDX. Factors affecting remediation performance were identified and optimized through the pilot test.

5.2.1 Period of Operation

The ZVI ISTW system was installed in August 2004 and was monitored until August 2005.

5.2.2 Performance Monitoring (Phase 3)

During the 12-month period of operation, three synoptic sampling events were conducted.

November 2004
April-May 2005
July 2005

Due to the intermittent operation of the ISTW, an assessment of long term operation was not possible. However, as discussed below, during the April/May 2005 period, we were able to demonstrate that groundwater concentrations of explosives were reduced to performance objective levels in a relatively-short (i.e., 10-day) period, indicating good hydraulic performance.

5.3 Data Analysis, Interpretation, and Evaluation

5.3.1 Groundwater Pumping Test

In September 2004 a pumping test was conducted to evaluate the performance of one of the ISTW. Water was pumped from the upper well screen of the “southeast” ISTW and injected into the lower screen at a rate of ~4 liters per minute. The data in Figure 5.1 show that water level changes in the well screens were on the order of 10-25 cm. Water level changes measured in the aquifer were less than 1 cm. As discussed in Section 3.6.4, the measured aquifer drawdowns were less than had been anticipated based on measured hydraulic conductivity values.

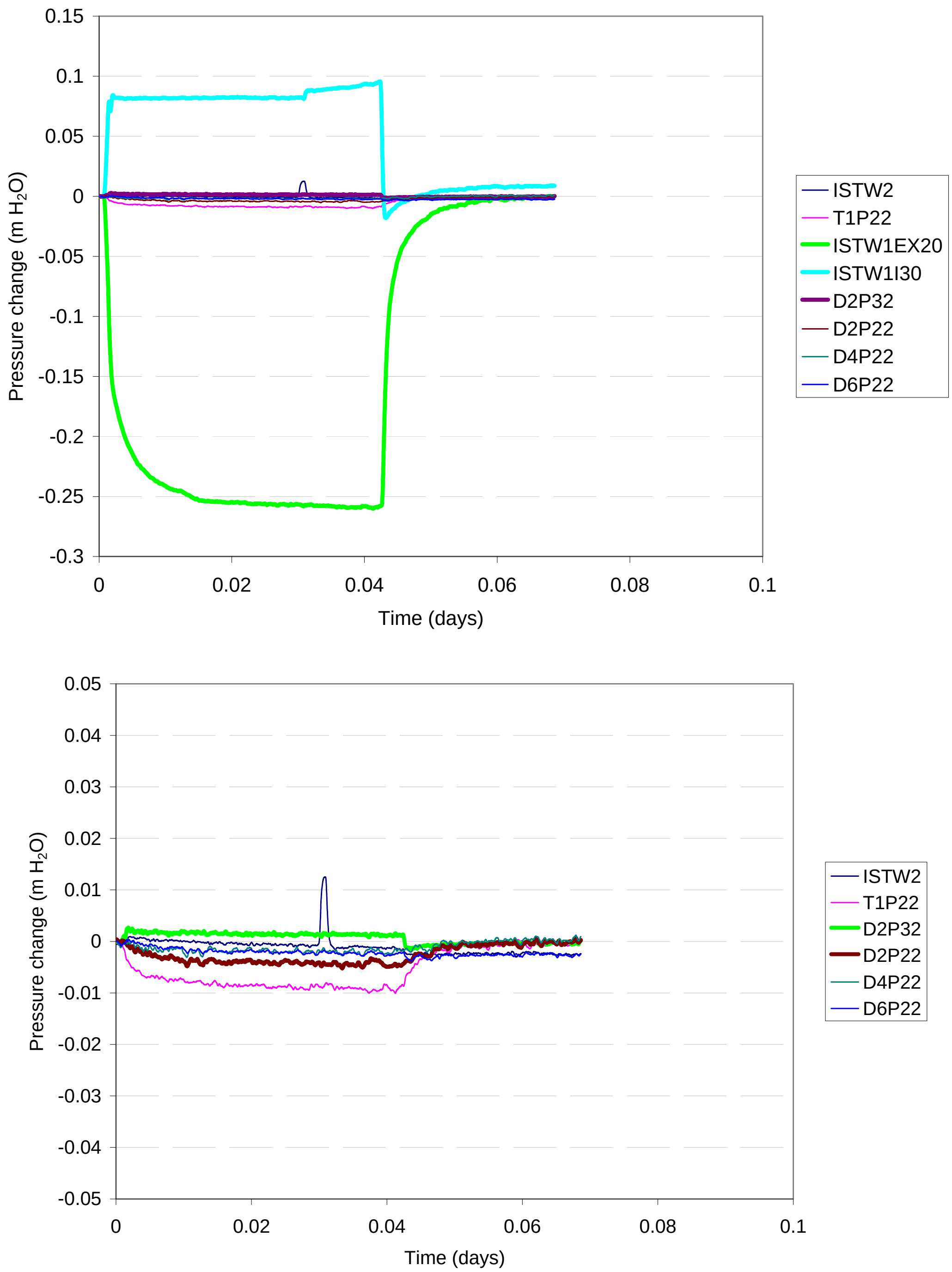


Figure 5-1. Pressure Change Observed During the Pumping Test.

5.3.2 Explosives concentrations in groundwater

For the 2-month period prior to May 2005, the ISTW system was inactive because of pump and power requirement issues. In May 2005, in conjunction with the tracer test described above, the concentrations of explosives in groundwater were monitored during a 2-week period of ISTW operation. During that period, a flow rate of 4 liters per minute was maintained in both ISTW wells. As a result of ISTW inactivity, the groundwater concentrations of explosives were at pre-ISTW values. The data in Table 5-2 show that over the 15-day period both TNT and RDX concentrations were substantially reduced throughout the treatment area. Only in the lower portion of D6 were concentrations not reduced below target levels, and we believe that this would have been achieved within another few days. It should also be noted that concentrations within the ISTW wells were always below the minimum quantitation limit, indicating that complete removal of the explosives was achieved using less than half of the treatment flowpath (i.e., water is treated both entering and leaving the ISTW, and complete removal was achieved after only the inflow portion of the flowpath.)

Table 5-2. Explosives Data During the May 2005 Pumping Period.

I.D.	Depth (m)	TNT (μg/L) *			
		4-May-05	7-May-05	14-May-05	19-May-05
		0	3	10	15
D2R	9.1-9.7	23.0	10.0	1.0	0.1
D2Y	7.9-8.5	56.0	9.0	0.5	0.1
D2G	6.7-7.3	137.0	43.0	0.6	0.1
D2B	5.5-6.1	122.0	69.0	3.0	0.1
D4R	9.1-9.7	33.6	7.6	0.3	0.1
D4Y	7.9-8.5	4.0	7.9	0.3	0.1
D4G	6.7-7.3	109.5	48.0	1.1	0.1
D4B	5.5-6.1	129.9	133.5	4.1	0.1
D6R	9.1-9.7	12.3	1.1	7.0	3.3
D6Y	7.9-8.5	44.5	14.7	5.3	2.0
D6G	6.7-7.3	21.7	38.8	0.2	0.2
D6B	5.5-6.1	161.2	121.3	1.2	0.7
T2R	9.1-9.7	26.2	17.3	0.2	0.1
T2Y	7.9-8.5	16.5	1.3	0.8	0.1
T2G	6.7-7.3	25.1	76.4	0.2	0.1
T2B	5.5-6.1	23.6	89.9	0.1	0.1

* minimum quantitation limit 0.1 μg/L

I.D.	Depth (m)	RDX (μg/L) *			
		4-May-05	7-May-05	14-May-05	19-May-05
		0	3	10	15
D2R	9.1-9.7	0.6	0.5	0.1	0.1
D2Y	7.9-8.5	1.1	0.4	0.1	0.1
D2G	6.7-7.3	0.9	0.3	0.1	0.1
D2B	5.5-6.1	1.4	0.1	0.1	0.1
D4R	9.1-9.7	0.7	0.5	0.1	0.1
D4Y	7.9-8.5	1.6	0.4	0.1	0.1
D4G	6.7-7.3	1.1	0.3	0.1	0.1
D4B	5.5-6.1	1.6	0.1	0.1	0.1
D6R	9.1-9.7	0.2	0.4	0.1	0.1
D6Y	7.9-8.5	0.5	0.7	0.1	0.1
D6G	6.7-7.3	1.1	0.4	0.1	0.1
D6B	5.5-6.1	0.5	0.1	0.1	0.1
T2R	9.1-9.7	0.6	0.8	0.1	0.1
T2Y	7.9-8.5	0.2	0.6	0.1	0.1
T2G	6.7-7.3	0.3	0.4	0.1	0.1
T2B	5.5-6.1	0.5	0.1	0.1	0.1

* minimum quantitation limit 0.1 μg/L

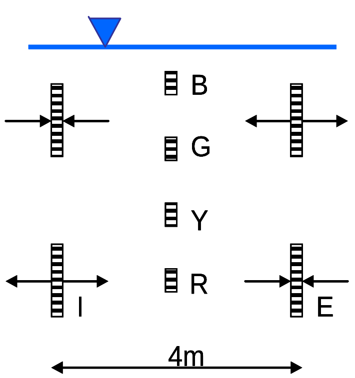
5.3.3 Bromide flow tracer test

In May 2005 (i.e., 9 months after installation) a bromide tracer test was conducted to evaluate flow around the ISTW system. Bromide was injected for a 4-hour period into the deep well screen of ISTW1 and water was circulated water was circulated between the ISTW pair for a ~2-day period, with 4 liters per minute being injected/extracted from each well screen. The data in Figure 5-2 show the flow and monitoring configurations, as well as the measured bromide concentrations.

a)

	Time (days)					
	0	0.1	0.3	0.6	1.3	2.1
D2R	3		9	11	8	7
D2Y	2		7	9	7	6
D2G	1		5	6	5	4
D2B	1		5	5	5	4
D4R	2		8	7	8	8
D4Y	2		7	7	6	5
D4G	1		8	5	5	5
D4B	1		6	4	4	3
D6R	2		8	6	6	7
D6Y	2		8	6	6	6
D6G	1		5	4	4	4
D6B	1		4	4	4	4
T2R	2		14	7	7	6
T2Y	1		12	6	6	6
T2G	1		9	4	4	4
T2B	1		6	3	3	3
INJECTION	2	972	136	26	26	18
NW WELL	2		13	11	14	12

b)



c)

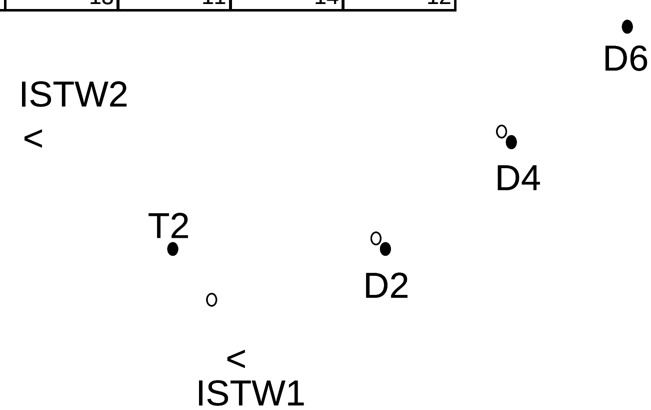


Figure 5-2. a) Data from the ISTW bromide tracer test; b) Cross-section view of the tracer layout; c) Plan view layouts of the ISTW system.

5.3.4 Numerical transport modeling of the bromide tracer test.

Using the numerical model discussed in Section 3.6.4, movement of bromide during the ISTW tracer test was simulated. Figure 5-3 shows the results of those simulations, and indicates that, while modelled concentrations were similar to measured values, peak concentrations at the monitoring points closest to the injection screen (R and Y) show concentrations that are less than predicted by the model while the well screens above them (G and B) respond more quickly than predicted by the model. The most likely explanation for this is that there is more vertical flow (short-circuiting) between the two well screens on each ISTW in the field than is predicted by the model. No adjustment of hydraulic conductivity values was made for this simulation. Relatively large values for horizontal and vertical dispersivities (1m and 0.1m, respectively) were used in this simulation.

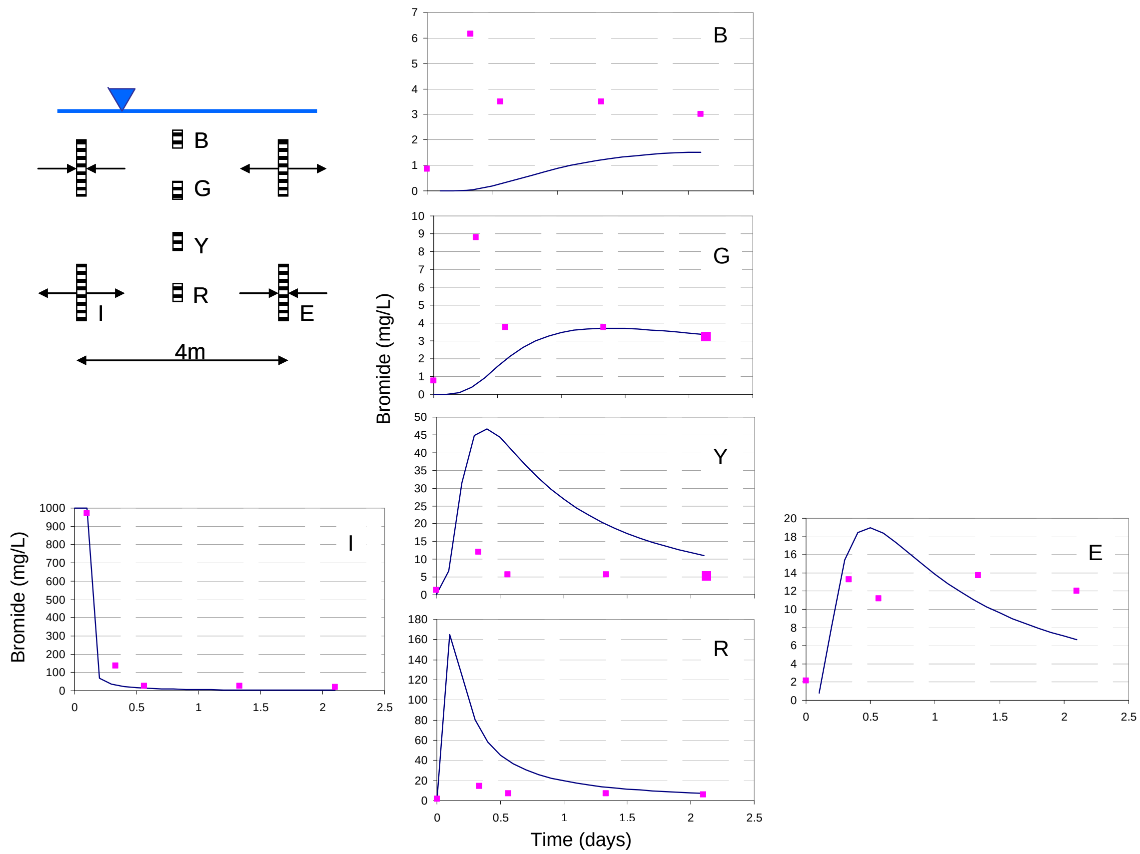


Figure 5-3. Numerical Transport Simulations (lines) **and Measured Bromide Concentrations** (pink squares) **for Location T2 During the ISTW Tracer Test.**

5.3.5 Post-operation performance assessment

The original project plan called for ~1 year of monitoring of the ISTW. Following installation of the wells and solar power system in August 2004 the system operated successfully during our site work (August and early September). However, in the period prior to the next scheduled sampling (November), the solar system failed to generate sufficient power to maintain pumping operations, and the system shut down. The system was re-started in November, but failed within a few days due to lack of power.

The system had been professionally designed by the manufacturer to meet our power needs, but it proved not to be adequate following multiple cloudy days. In addition, a stand-alone system to control the data acquisition system should have been included in the design to insure that control and data acquisition systems would continue operation and allow for system re-start when sufficient power was available.

An unexpected aspect of ISTW operation was that essentially all electrical components placed in the wells failed. This included electrical pumps and pressure transducers. These failures were clearly due in some way to the strongly reducing geochemical conditions in the well. Beginning in the spring of 2005, all of those components were replaced with ones that did not require electricity in the well, including pneumatic bladder pumps and water-level sensors that used air pressure in tube placed below the water table to measure water levels in the wells.

Finally, and most importantly, from the perspective of long-term operation, hydraulic performance of the wells decreased over time once sustained operations were maintained. It was anticipated that plugging might occur at the influent screens as water containing dissolved oxygen entered the ISTW. The system had been designed to take this into account, and indeed, this was not where the failure occurred. Instead, the injection well screens became plugged as a result of oxygen entrained in the water due to mixing in the well bore. In retrospect, this problem could have been minimized by placing a packer in the well above the screen to eliminate contact with air in the well bore. Another potential source of the plugging was that water levels in the surrounding aquifer dropped subsequent to installation of the ISTW. As a result, when the wells were not in operation, and particularly when the shallow screen was used for extraction, a portion of the ZVI was above the water table, and became plugged. This too could have been avoided if the wells screens were placed deeper below the water table.

The bottom line with regard to performance of the ZVI ISTW is that they are probably too prone to failure to be widely utilized. However, given the rapid reaction rates for reduction of explosives, the approach is still an attractive for groundwater contamination plumes that can not be addressed by conventional PRB. It should be possible to operate ISTW with ZVI "cartridges" within the well bore. This would allow the cartridges to be replaced when necessary.

6. COST ASSESSMENT

This section discusses cost considerations involved in the application of ISTW to remediate explosives in groundwater.

6.1 Summary of treatment costs for the demonstration

Groundwater treatment and monitoring costs incurred during the CAAP ISTW demonstration are shown in Table 6.1. Only costs associated with the treatment of groundwater are included. Costs associated with validation of the technology are not included. All of the costs are based on best available estimates.

Table 6-1. Summary of Treatment Costs.

Item	Sub-Total ($)	Total Cost ($)
Pre-installation		
Site characterization	$50,000	
Bench-scale tests	$10,000	
Engineering Design	$25,000	
Materials (iron)	$2,000	
ISTW Construction		
Site preparation and ISTW installation	$80,000	
Solar powered pumping system	$20,000	
Monitoring Network	$10,000	
Disposal of spoils	$0	
Total ISTW Construction Costs		**$197,000**
Maintenance costs (20 months)	$0	
Groundwater Monitoring	$20,000*	
Total Operation and Maintenance Costs		**$20,000**
Total Demonstration Cost		**$217,000**

*This value is greater than the actual value because much of this work was conducted concurrently with the CAAP PRB project. The costs reported here reflect the total cost if the two projects had not been carried out concurrently.

6.2 Summary of validation costs for the demonstration

In addition to the costs described in section 5.1, there were a number of additional costs that fall in the area of validation, rather than demonstration. (We believe this is the case because they do not directly involve the project performance criteria.) These activities were deemed necessary in order to meet peer-reviewed science standards.

Table 6-2. Summary of Validation Costs for the ISTW Demonstration.

Item	Sub-Total ($)	Total Cost ($)
Hydraulic conductivity characterization	$20,000*	
In situ reactivity testing	$20,000	
Other validation costs (pumping and tracer tests)	$40,000	
Total validation costs		**$80,000**

6.3 Scale-up recommendations

6.3.1 Options for design of full-scale barriers for explosives

Zero-valent iron is extremely effective at degrading explosives in groundwater. In that context, the design of the ISTW was more than required to meet the needs of the site. Hydraulic performance within the aquifer met expectations based on pre-installation site characterization. Expansion from two to multiple ISTW is straightforward. If adjacent wells operate in opposite directions (i.e., extraction in the upper screen, next to extraction in the lower screen) then a line of ISTW can be repeated indefinitely. Because both pumping and treatment occur at each individual ISTW, unit costs for treatment are not expected to change with size. (Of course, there will likely be some cost savings for well installation because mobilization costs will be divided amongst a larger number of wells.)

7. IMPLEMENTATION ISSUES

7.1 Cost Observations

The majority of the costs associated with this ZVI ISTW implementation are associated with installation of the wells. For this demonstration the costs per well was ~$40,000. It is anticipated that this could be reduced if a larger number of wells were installed. However, this will also be a function of the depth associated with the groundwater contamination to be treated. Monitoring costs were considerably higher than would be the case at a full-scale installation because of the detailed multi-level samplers installed at the demonstration site.

7.2 Performance Observations

Although the performance objectives of this project were largely met, this demonstration can not be considered a success because long-term performance was not able to be demonstrated. This occurred for a number of reasons, including: 1) the solar power system could not deliver consistent pumping during extended periods of overcast skies; 2) all of the down-hole electronic equipment failed as a result of corrosion (this included pumps, water level transducers and flow transducers); and most importantly 3) there was a loss of permeability of the iron in the iron due to introduction of oxygen in the upper screened interval. We believe that all of these could have been eliminated if they had been anticipated and addressed. With regard to item 3, we had initially been concerned that mineral precipitation (particularly sulfides from sulfate reduction) would plug extraction well screens, however, this does not appear to have occurred and the primary reason for plugging was due to oxygen. Oxygen was introduced into the upper well screens in two ways. In the well where water was extracted from the upper screen, regional lowering of the water table due to drought conditions, coupled with pumping from the well, caused a portion of the iron to become exposed to the atmosphere. This process led incrementally to loss of permeability in the iron. (If the screened interval were maintained below the water table, it is anticipated this would not have been a problem). Oxygen was introduced into the well with the upper injection screen due to contacted of the water within the well bore with air above the water table. This could again have been eliminated if the screen was installed below the water table, and if a packer were placed in the well between the static water level and the top of the screen. Alternately, if this technology were to be tested again, it would be advisable to design a “cartridge” system in which a large diameter dual-screened well (e.g., 12-18 inch diameter) was installed and removable cartridges containing the iron could be positioned at the well screens.

7.3 Regulatory Issues

Regulatory issues did not pose any problems for this demonstration. However, our ability to use direct-push wells was contingent on the fact that we were located on a federal facility, and thus

did not have to comply with current state regulations about the construction of wells. State of Nebraska regulators were very helpful in this context; however, this may not be the case in other states where current regulations do not reflect changing understanding of the role of direct-push wells.

7.4 Research Needs

Based on the performance objectives discussed above, modifications to the design of the ISTW would need to be evaluated in order to demonstrate the effectiveness of the technology. We believe that the reactivity of the iron is sufficient to remove explosives from the groundwater for an extended period. Thus, the primary issues in need of further research would relate to the hydraulic performance of the iron, and well designs that would enhance long-term performance

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9. POINTS OF CONTACT

A summary of contact information for all personnel associated with this demonstration project is presented in Table 9-1.

Table 9-1. Project Team Points of Contact.

Point of Contact	Organization	Phone	email	Role
Rick Johnson	OHSU	(503) 748-1193	rjohnson@ebs.ogi.edu	PI Project Manager
Paul Tratnyek	OHSU		tratnyek@ebs.ogi.edu	Co-PI